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Electrical conduction in semiconducting CuO-Bi_2O_3 Pellets

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Abstract : The electrical conductivity and dielectric constant are very interesting properties, which provides important information regarding the conduction mechanism in solids These properties give an idea about the internal transport mechanism, structure and some new insights too. The electrical properties such as dc-conductivity and dielectric constant, variation with temperature for three different composition of CuO-Bi_2O_3 pellets (which are pressed at 100°C) have been reported A plot of $-\log \sigma$ versus $1/T$ shows two different regions of conduction and suggests that two types of conduction mechanisms are involved and switching of one type to another occur at knee temperature (θ_c)

Activation energy calculated for both regions (LTR and HTR) is below 1 eV, thus the electrical conduction is electronic. Non adiabatic hopping conduction was observed in the samples. A plot of dielectric constant *versus* log of frequency is of zig-zag nature. Dielectric constant decreases with increase of mol % of CuO. The dielectric constant of pellets is temperature dependent.

Keywords : CuO-Bi_2O_3 pellets, conductivity, dielectric constant, non adiabatic hopping conduction.

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1. Introduction

The studies on electrical conduction in glasses started in 1955 revealed several important features of semiconducting glasses. The transition metal oxide glass shows semiconducting behaviour because of transition metal ions. The first report on measurements on dc-conductivity of transition metal oxide glasses have been given by Denton *et al* [1] with 90 mole percent V_2O_5. Ghosh and Chaudhuri [2] discussed the dc-conductivity of semiconducting vanadium bismuth oxide containing 80-95 mol % vanadium pentoxide in the 300-500 K temperature range. They observed the adiabatic hopping conduction and discussed results of measurements on the basis of polaronic hopping model.

Singh and Tarsikka [3] have measured dc-conductivity of six samples of sodium-cuprous phosphate glasses. The activation energy has been evaluated and the possibility of ionic or electronic conduction is discussed. The hopping transport phenomenon in bismuth-borate glasses is discussed on the basis of bismuth ions by Yawale [4]. Many research workers [2,5] have reported the transport properties of semiconducting glasses, but less attention have been given on the powder pressed pellets of the glasses. It is our endeavour to observe behaviour of the various transport properties of the pellets and compare with the properties of glasses of same compositions so as to get new insight about the conduction mechanism, structure etc.

In the present work, it is decided to measure the variation of dc-electrical conductivity with temperature. Similarly the variation of dielectric constant with frequency and temperature is also studied with an intention to know the conduction mechanism and relaxation effects in CuO-Bi_2O_3 pellets

Gawande *et al* [6] have been observed the adiabatic hopping conduction in CuO-Bi_2O_3 pellets (pressed of 50°C) showed that it is mainly controlled by activation energy.

2. Experimental

2.1. Preparation of the samples :

Pellet samples under investigation were prepared in the laboratory by mixing an appropriate amount of CuO and Bi_2O_3 (mol %), Anala R grade chemicals. A homogeneous mixture of two powders was prepared and fired in a fire-clay crucible at 1000°C ± 10°C for half an hour in an automatically temperature controlled muffle furnace. Then the molten mixture was taken out, allowed to cool and crushed into powder form. The powder was then pressed on the pellet machine having pressure 3×10^3 kg/cm^2 with the binding reagent euprol at 100°C in circular shape having diameter 2 cm and thickness 0.2 cm. A thin conducting silver paint in a circular form is pasted on the opposite sides of the sample for the purpose of electrical measurements. Heat treatment is given to all silver painted samples at 100°C for fixing the paint and removing the air bubbles.

The amorphous nature of the sample was checked by X-ray diffraction method.

2.2. Electrical measurements :

The resistance of the pellet was measured by voltage drop method given by Kher and Adgaonkar [7] and Yawale [4]. The voltage measurements across the standard resistance was measured by using Digital multimeter DT-850, Japan having accuracy of ± 1 mV. The resistance of the pellets of various compositions was measured at constant voltage (600 V) in the temperature range 343 K to 539 K. The accuracy in the resistance measurement was less than 2%.

The dielectric constant of the pellets was measured by measuring the capacity using Radart LCR Bridge type 5102 at different frequencies, at room temperature (300 K) and also at 1 KHz frequency in the temperature range 303 K to 623 K.

3. Theory

The dc-conductivity of semiconducting oxide glasses for the hopping of polarons in non-adiabatic approximation is given by [8,9]

$$\sigma = \frac{\nu_0 N e^2 R^2}{kT} C(1-C) \exp(-2\alpha R) \exp(-W/kT), \tag{1}$$

where

C – the fraction of reduced valence sites of the transition metal ions,

ν_0 – the frequency factor,

N – number of metal ion sites per unit volume,

R – hopping distance and,

W – activation energy.

The term exp (- αR) represents electron overlap integral between sites.

Assuming that a strong electron lattice interaction exists, the activation energy W is the result of polaron formation with binding energy W_P and any energy difference W_D which might exist between the initial and final sites due to variation of the local arrangements of ions

Austin and Mott [8,9] have shown that

$$\begin{aligned} W &= W_H + (1/2)\, W_D \quad \text{for } T > \theta_D/2\,, \\ &= W_D \quad \text{for } T < \theta_D/4, \end{aligned} \tag{2}$$

where,

W_H - polaron hopping energy,

W_D - disorder energy arising from the energy difference between two neighbouring hopping sites and

θ_D - Debye temperature.

The polaron hopping energy W_H is given by

$$W_H = W_P/2, \tag{3}$$

where,

W_P - polaron binding energy.

To check the nature of hopping conduction (adiabatic or non-adiabatic) mechanism, three methods have been suggested.

(I) The first method suggested by Sayer and Mansingh [10] and Murawaski *et al* [11] is adopted. When the overlap integral between sites $J_0 \exp(-\alpha R)$ approches to J_0 *i.e.* $\exp(-\alpha R) \rightarrow$ unity, the hopping is adiabatic and it is mainly controlled by the activation energy.

The dc-conductivity is given by

$$\sigma = \left(\nu_0 N e^2 R^2/kT\right) C(1-C) \exp(-W/kT). \tag{4}$$

To explore the nature of hopping conduction, a plot of log σ versus activation energy W at fixed temperature for pellets of different compositions is to be plotted. If this plot shows a straight line nature, then it indicates that eq. (4) is valid. This plot gives slope equal to $1/kT$ and intercept on log σ axis gives the value of constant A, where,

$$A = \log\left(\nu_0 N e^2 \; R^2/kT\right) C(1-C).$$

From the slope (plot of log σ *versus* activation energy) $1/kT$, the value of temperature is estimated. If the estimated temperature is found to be nearly equal to temperature (K) taken, then the hopping conduction is adiabatic in nature and it is mainly controlled by the activation energy.

If the eq. (4) is not valid, the value of estimated temperature from the plot and the fixed temperature taken will be very different, then this will suggest that the nature of hopping conduction is non-adiabatic.

(II) In the second method, the polaron band-width J should satisfy the inequality suggested by Holstein [12]

$$J \gtrless \left(2kTW_H/\pi\right)^{1/4} \left(\hbar\,\omega_0/\pi\right)^{1/2} > \text{ for adiabatic}$$
$$< \text{ for non adiabatic.} \tag{5}$$

The polaron bandwidth J can be estimated

$$J \sim e^3 \left[N\left(E_F\right)\right]^{1/2} / \varepsilon_P^{3/2}, \tag{6}$$

where $$\frac{1}{\epsilon_p} = \frac{1}{\varepsilon_\infty} - \frac{1}{\epsilon_S},$$

ε_∞ - high frequency dielectric constant,

ε_s - low frequency dielectric constant.

$N(E_F)$ - density of states at Fermi level or J can be estimated from

$$J \approx \exp(-\alpha R)$$
$$J = J_0 \exp(-\alpha R). \tag{7}$$

(III) The third method has been suggested by Friedman and Holstein [13,12] who derived an expression for the mobility in case of non-adiabatic hopping

$$\mu = (3/2)\left(eJ^2R^2/kT\right)\left(\pi/kT\,W_H\right)^{1/2} \exp\left(-W_H/kT\right), \tag{8}$$

and Emin and Holstein [14,12] derived an expression for the mobility, in case of adiabatic hopping

$$\mu = (4/3)\left(e\omega_0R^2/kT\right) \exp\left[\left(J - W_H\right)/kT\right]. \tag{9}$$

4. Results and discussion

The variation of dc-conductivity with temperature for the different compositions of CuO and Bi_2O_3 pellets is shown in Figure 1. For all the samples, dc-conductivity follows the Arrhenius relation

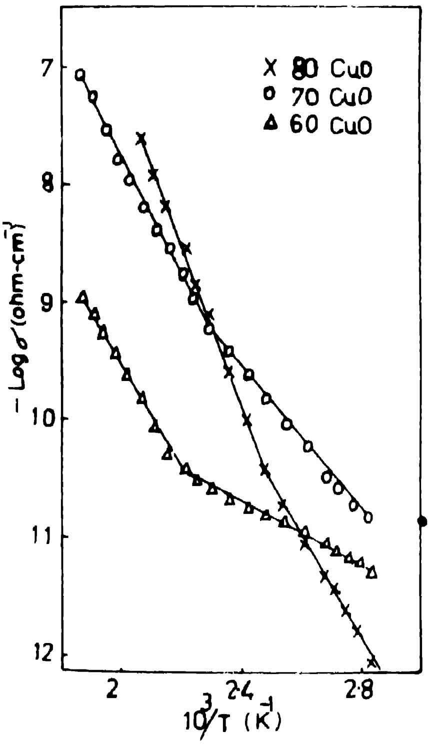

Figure 1. Variation of dc-conductivity ($-\log\sigma$) *versus* $1/T$, for the pellets of different compositions of CuO-Bi_2O_3.

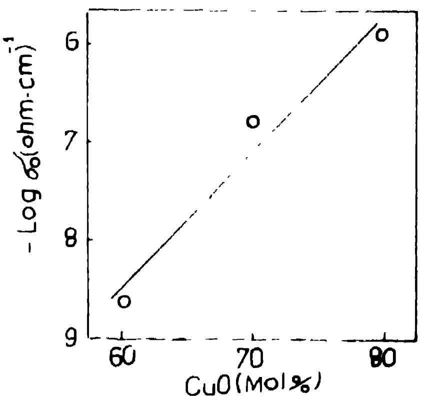

Figure 2. Variation of pre-exponential factor ($-\log\sigma_0$) with compositions of CuO mol %

$$\sigma = \sigma_0 \exp\left(-W/kT\right),$$

where σ_0 (ohm-cm)$^{-1}$ is the pre-exponential factor. W (eV) the activation energy, $T(K)$ the temperature and k the Boltzman constant. The conductivity increases with increase in temperature and also with mol % of CuO. This plot contains two regions of temperature (343 K to 453 K) and (453 K to 533 K). In region I (343 K to 453 K) conductivity varies with temperature linearly but increase in conductivity with temperature is slow. In temperature region II (453 K to 533 K) the variation of conductivity with temperature is linear but the conductivity increases rapidly with temperature. The activation energy from the slope of the straight line (Figure 1) in both the regions is calculated and it is observed that activation energy is temperature independent but depends on composition. The activation energy calculated is found to be of the order of glasses in general [4,5].

Plot of $-\log \sigma$ *versus* $1/T$ (Figure 1) suggests that, in these pellets two types of conduction mechanism are present and switching of conduction from one type to other takes place at respective knee temperatures (θ_r).

The intercept of $-\log \sigma$ *versus* $1/T$ plot gives pre-exponential factor $-\log \sigma_0$. Figure 2 shows the plot of $-\log \sigma_0$ *versus* CuO mol % for all the pellets. The nature of the curve is linear, and the pre-exponential factor increases with the increase of CuO concentration.

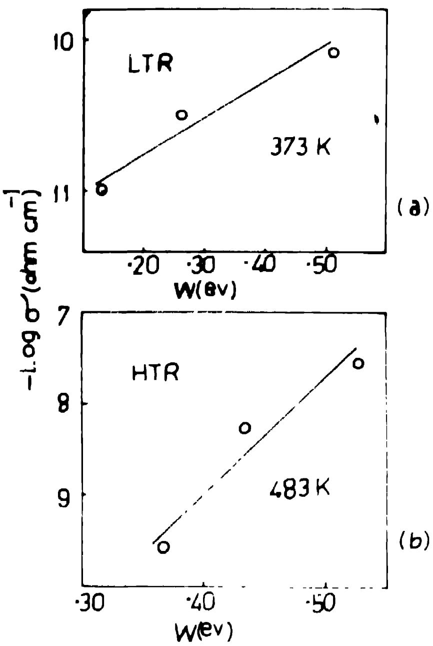

Figure 3. Plot of electrical conductivity ($-\log \sigma$) *versus* activation energy (W) at fixed temperature (exploration of eq. (4) · (a) LTR (373 K), (b) HTR (483 K))

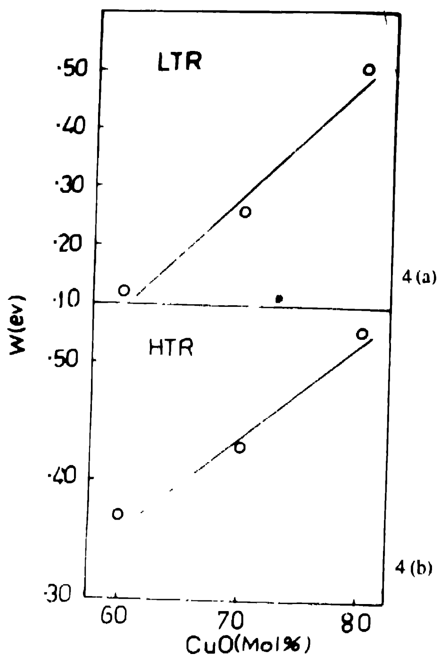

Figure 4. Dependence of activation energy (W) on composition of CuO mol % in (a) LTR, (b) HTR

To examine the nature of hopping conduction, the method suggested by Sayer and Mansingh [10] and Murawaski *et al* [11] is adopted. The exploration of eq. (4) is done by plotting $-\log \sigma$ against activation energy W (eV) at fixed temperature, showing straight line nature, but the temperature estimated (476 K) from the slope (Figure 3a) is found to be very different from the fixed temperature taken (373 K) in LTR. Similarly, for HTR (Figure 3b) estimated temperature (772 K) is different from the fixed temperature taken (483 K). This indicates that the hopping conduction is non-adiabatic in nature in both LTR and HTR. Therefore, the conduction is not mainly controlled by the activation energy.

The activation energy W is plotted against CuO mol % for the two temperature regions (HTR and LTR). Figures (4a) and(4b) shows linear nature with CuO mol % and activation energy increases with the increase in CuO mol %. All the samples studied indicated a negative temperature coefficient as well as electronic conduction, since the activation energy is less than 1 eV.

The plot of $-\log \sigma$ *versus* $1/T$ (Figure 1) divided into two linear regions from some fixed temperature called knee temperature (θ_t). This knee temperature is plotted against CuO mol % (Figure 5). This linear plot indicates that the knee temperature decreases with the increase in CuO mol %. Sometimes, this knee temperature may be a glass transition temperature (T_g) at which softening of glass takes place and hence the change in structure of the glass.

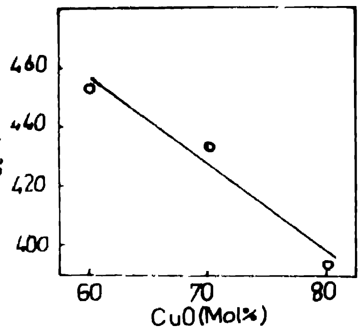

Figure 5. Plot of knee temperature (θ_t) *versus* composition of CuO mol %

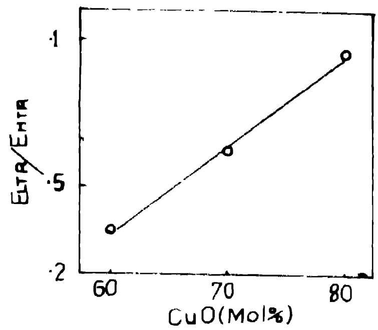

Figure 6. Plot of ratio of low to high temperature activation energy *versus* composition of CuO mol %

The ratio of low temperature to high temperature activation energy is plotted against CuO mol % (Figure 6). This plot shows that the ratio E_{LTR}/E_{HTR} increases linearly with the increase in composition of CuO mol %.

The dielectric constant (ε') of three samples studied is found to be frequency, temperature and composition (CuO) dependent. Figure 7 shows variation of dielectric constant with log of frequency at room temperature. The nature of the plot is zig-zag and shows dip at 1 KHz frequency for all the samples. This zig-zag nature of the curve is probably due to relaxation effects.

This type of behaviour is well known in amorphous materials and is due to distribution of relaxation times arising from local disorder.

Figure 8 shows the variation of dielectric constant with temperature (303 K to 623 K) for all the pellets at frequency 1 KHz. It is observed that the dielectric constant is independent of temperature upto 383 K and beyond 383 K, it increases rapidly. This increase in dielectric constant is due to a change in electronic structure and partly due to thermal expansion. The dielectric constant ε' of all the three pellets at room temperature is found to be of the order of

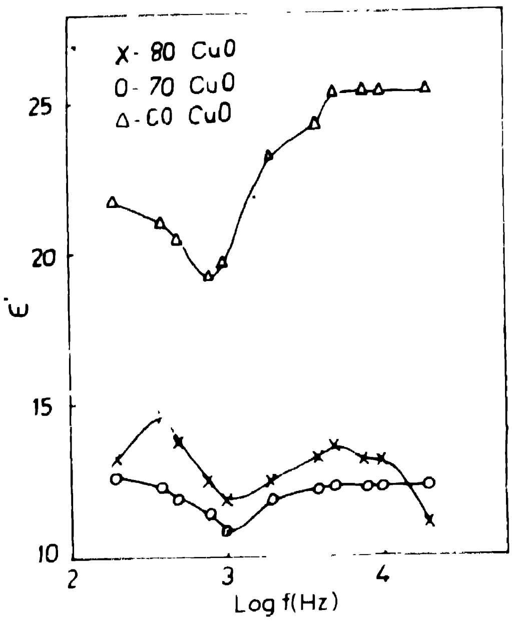

Figure 7. Variation of dielectric constant (ϵ') with frequency at room temperature (300 K) for different composition of CuO and Bi_2O_3

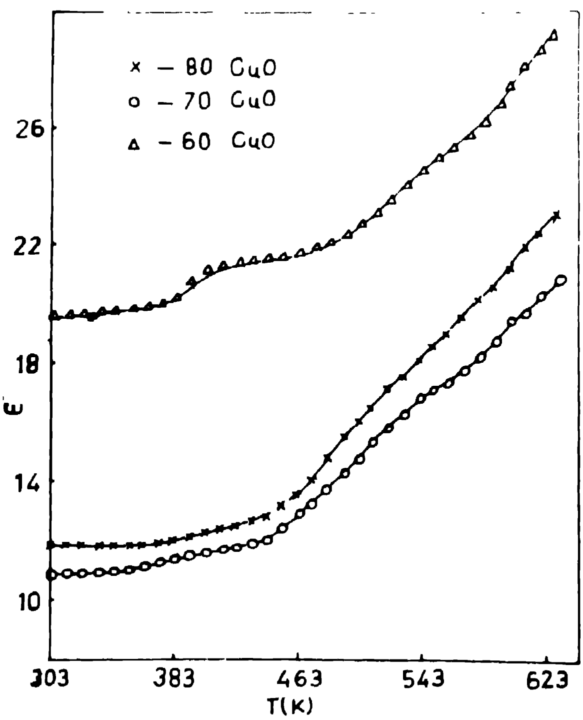

Figure 8. Variation of dielectric constant (ϵ') with temperature (303 K to 623 K).

values of ε' for glasses appearing in the literature [15]. The change in dielectric constant at high temperature is a characteristics of Debye-type relaxation process where symmetrical distribution of relaxation time takes place.

In Figure 9, the plot of dielectric constant versus mol % of CuO at three different frequencies 0.2 KHz, 1 KHz and 10 KHz, shows that the variation of dielectric constant with

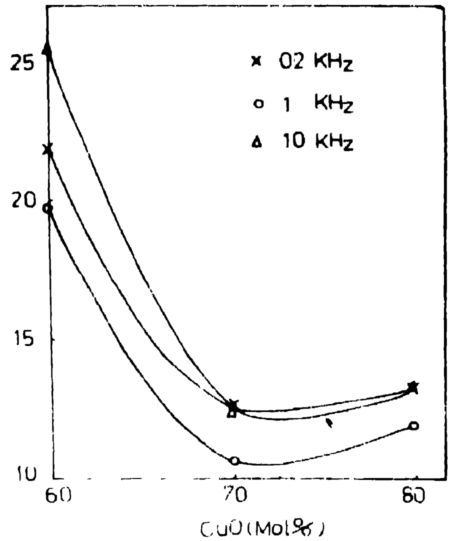

Figure 9. Variation of dielectric constant (ε') with composition of CuO mol % at different frequencies

CuO mol % is not systematic. The value of dielectric constant is found to be less for 70 CuO (mol %) pellet than 60 and 80 CuO (mol %).

5. Conclusion

The variation of $-\log \sigma$ *versus* $1/T$ is linear as observed in the case of many semiconducting glasses. Non-adiabatic hopping conduction is observed suggesting that the conductivity is not mainly controlled by the activation energy. The activation energy is found to be less than 1 eV, thus the conduction is electronic. In these pellets, dipole relaxation phenomenon is observed The dielectric constant of the pellets is found to be temperature, frequency and composition dependent.

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References

[1] E P Denton, H Rawson and J E Stanworth *Nature* **173** 1030, 4413 (1954)

[2] A Ghosh and B K Chaudhuri *Indian J. Phy* **58A** 62 (1984)

[3] B Singh and R S Tarsikka *Indian J Pure Appl. Phys* **27** 290 (1989)

[4] S P Yawale *Ph. D. thesis* (1992) (Amravati University, Amravati)

[5] A R Kulkarni, H S Maithi and A Paul *Bull. Mater. Sci.* **6** 216 (1984)

[6] W J Gawande, D K Burghate, S G Motke, S V Pakade and S P Yawale *J. Mater Sci (UK)* (Communicated) (1994)

[7] V G Kher and C S Adgaonkar *Indian J Pure Appl Phys.* **10** 902 (1992)

[8] I G Austin and N E Mott *Adv Phys* **18** 41 (1969)

[9] N F Mott *J. Non-Cryst Solids* **1** 1 (1968)

[10] M Sayer and A Mansingh *Phys. Rev.* **B6** 4626 (1972)

[11] L Murawaski, C H Chung and J D Meckenzie *J. Non-Cryst. Solids* **32** 91 (1979)

[12] T Holstein *Ann Phys* **8** 343 (1959)

[13] L Friedman and T Holstein *Ann Phys.* **21** 494 (1963).

[14] D Emin and H Holstein *Ann Phys* **53** 4391 (1969)

[15] A R Van-Hipple *Dielectric Materials and Applications* (London : Chapman and Hall) p 309 (1954)